

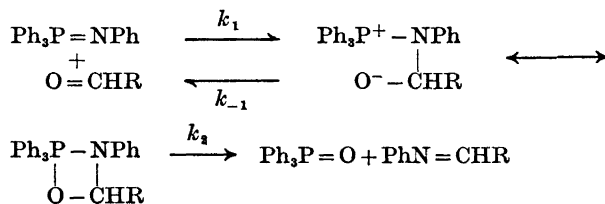
Kinetic Study of the Reaction Between Phosphine Imines and *p*-Nitrobenzaldehyde

PAUL FRØYEN

Chemical Institute, University of Bergen, Bergen, Norway

The reaction between *p*-nitrobenzaldehyde and a series of phosphine *N*-phenylimines has been studied in benzene. Some rate measurements were also performed in acetone, dimethyl formamide, and dimethyl sulphoxide. The reaction is first order in each of the phosphine imine and aldehyde. The rates show little dependence on the polarity of the solvent. This finding is inconsistent with the proposed intermediacy of a betaine. However, in hydrogen bonding solvents, the rate of the reaction is highly increased. The influence of the phosphorus substituents on the rate and course of the reaction is discussed.

It has long been known that phosphine imines react with carbonyl compounds to give phosphine oxides and Schiff bases.¹ The reaction has been studied by several workers,²⁻⁶ and it is assumed⁷ that the mechanism parallels that of the Wittig reaction, in which phosphonium ylides convert aldehydes and ketones into olefins. Recently Johnson and Wong⁶ have shown this mechanism to be substantially correct by a kinetic study of the reaction between a series of triarylphosphine *N*-phenylimines and aromatic aldehydes.



Scheme 1.

The reaction was twice as fast in ethanol as in chloroform, and 30 times as fast in ethanol as in benzene. These observations were attributed to increased charge localization in the transition state of the reaction, that is, to the intermediacy of a betaine. Johnson and Wong⁶ conclude that the second step of the reaction, betaine decomposition, is the fastest when the *P*-phenyl groups

carries one of the substituents: *p*-CH₃, *p*-Br, and *p*-Cl, and when the *N*-phenyl group carries an electron withdrawing substituent. When the *N*-phenyl group carries an electron donating substituent, it was assumed that the rate controlling step changes from the betaine forming to the betaine decomposing step. No rate studies have been performed for phosphine imines with substituents other than aryl. In view of the results published by Johnson and Wong,⁶ it seemed of interest to study the influence of other substituents in the imines, especially of those linked to phosphorus, on the rate and course of the reaction. It has been generally accepted that electron donating groups linked to phosphorus lead to decreased reactivity in the second step, since they render the phosphorus atom in the betaine less susceptible to attack by the oxyanion.⁶ If this is so, strong electron donating substituents on phosphorus might be expected to change the rate controlling step of the reaction from a betaine forming first step to a betaine decomposing second step. The present author has undertaken a study of the reaction between *p*-nitrobenzaldehyde and a series of phosphine *N*-phenylimines in which the phosphorus substituents are triphenyl, diphenylethyl, phenyldiethyl, phenyl cyclohexylmethylene, and triethyl. The rate data are summarized in Table 2.

In order to shed further light on the mechanistic details, a study of the solvent effect on this reaction was undertaken. The rate increase observed in ethanol and chloroform⁶ might be due to the hydrogen bonding abilities of these solvents. The influence of a series of hydrogen bonding agents as phenol, thiophenol *etc.* was studied in benzene solution. In order to distinguish effects primarily due to hydrogen bonding from those due to increased polarity of the solvent, polar solvents which cannot form hydrogen bonds were also studied. Rate studies were performed in acetone, dimethyl formamide (DMF) and in dimethyl sulphoxide (DMSO). The results are summarized in Table 2.

EXPERIMENTAL

Materials

p-Nitrobenzaldehyde (Fluka *puriss.*) was recrystallized two times from ethanol, m.p. 106°, lit.⁸ 106°. The phosphine *N*-phenylimines were synthesized according to Staudinger⁹ from the respective phosphines and phenyl azide.

Triphenylphosphine N-phenylimine m.p. 135° (lit.⁹ 130–31°).

Ethyldiphenylphosphine N-phenylimine m.p. 79° (lit.¹⁰ 79°).

Phenyldiethylphosphine N-phenylimine m.p. 69° (lit.¹ 69–70°).

Triethylphosphine N-phenylimine, b.p. 120°/0.35 (lit.¹ 116°/0.008).

1-phenyl-1-phospholane N-phenylimine m.p. 88° (lit.¹⁰ 88°).

Benzene used as solvent was freed from thiophene by extraction with sulphuric acid. The product was neutralized with sodium carbonate and washed with water. After drying over calcium chloride, the product was fractionated from sodium.

Acetone. A product made for ultraviolet spectroscopy (E. Merck) was used as received after drying with molecular sieve.

Dimethyl sulphoxide was fractionated from calcium hydride, b.p. 70°/10, lit.¹¹ 71°/11.

Dimethyl formamide. A pure product was used as received (Fluka *puriss.*).

Kinetic measurements

The reaction between *p*-nitrobenzaldehyde and the phosphine *N*-phenylimines was studied in benzene. The rates of reaction of the various imines were determined by following the ultraviolet absorption of the reaction solution at the absorption maximum


of 4-nitrobenzylidene aniline at 350 μ . The rate constants were calculated as described in a previous communication.¹² The reaction of ethyldiphenylphosphine *N*-phenylimine was also studied in acetone, DMF, and DMSO. The catalytic effect of several hydrogen bonding compounds were studied in benzene. The rate of reaction of phenyldiethylphosphine *N*-phenylimine and 1-phenyl-1-phospholane *N*-phenylimine with methyl iodide was studied in deuteriochloroform by a PMR technique by following the methyl signal of the phosphonium salts formed.

RESULTS AND DISCUSSION

Rate data together with activation parameters for the reaction between *p*-nitrobenzaldehyde and the various phosphine *N*-phenylimines are recorded in Table 2. The data confirm earlier observations that the kinetics of the reaction show first order rate dependence in imine as well as in aldehyde, *i.e.* overall second order kinetics. As can be seen from Table 2, successive replacement of phenyl with ethyl on the phosphorus portion of triphenylphosphine *N*-phenylimine led to considerable increase in reaction rates. The rate increase is of the same order of magnitude as observed for triphenyl- and triethylphosphine fluorenylide in the reaction with *p*-nitrobenzaldehyde, about 3×10^3 .¹³ In accordance with the current view of the mechanism of this type of reactions, the rate increase should indicate that the first step, betaine formation, is rate determining, since the more nucleophilic phosphine imines react fastest. This view is based on the assumption that electron donating substituents, whether they are linked to phosphorus or nitrogen, are enhancing the first step of the reaction, whereas they are making the oxyanion attack on the phosphorus atom more difficult in the second step by decreasing the positive character of phosphorus. Thus, it is assumed that if $k_1 \sim k_2$ (Scheme 1), an increase in k_1 is more or less completely masked by a decrease in k_2 . In accordance with this view, Johnson and Wong,⁶ report reactions between *p*-nitrobenzaldehyde and a series of phosphine imines, where the more nucleophilic imines give slower reaction rates. The authors are of the opinion that in the reaction of the compound, $\text{Ph}_3\text{P}=\text{N}-\text{C}_6\text{H}_4\text{X}$, where $\text{X} = p\text{-NO}_2(\text{a})$, $m\text{-NO}_2(\text{b})$, $m\text{-Cl}(\text{c})$, $p\text{-Br}(\text{d})$, $\text{H}(\text{e})$, $p\text{-CH}_3(\text{f})$, and $p\text{-OCH}_3(\text{g})$, the rate determining step changes from betaine formation in the imines (a)–(e) to betaine decomposition in (f) and (g). This is indicated by a Hammett plot of $\log k/k_0$ versus σ . The phosphine imines (a)–(e) give a straight line with a ρ value of -2.4 , whereas (e)–(g) give a ρ value of $+0.95$. On the basis of these findings, the authors conclude that especially in the reaction of (e) there is only a small difference in the rates of the two steps. In view of the above-mentioned kinetic data it was expected that replacement of *P*-phenyl groups in (e) with alkyl groups would change the rate determining step to betaine decomposition. Accordingly, a rate decrease ought to be expected to accompany this substitution. However, as can be seen from Table 2, the latter assumption is strongly contrasted by the experimental findings in the present investigation. Although there is no evidence on this point, it is assumed by the present author that the first step of the reaction is reversible. This seems probable since in the analogous Wittig reaction there is strong evidence for the reversibility of the first step. Following this assumption it seems reasonable to expect an increase in k_1 (Scheme 1) and a decrease in k_{-1} and k_2 as the phenyl groups

linked to phosphorus are replaced with ethyl groups. The 3×10^3 rate increase from triphenyl- to triethylphosphine *N*-phenylimine may thus indicate that the substitution has a more dominant effect on the equilibrium between reactants and intermediate than on the reactivity in the second step. The phospholane derivative (4) reacts about 10 times faster with *p*-nitrobenzaldehyde than does (3), which has comparable inductive substituent effects. If a minor steric effect is ignored, this rate increase can be attributed to the "phospholane effect."¹⁴ The "phospholane effect" will come into play if $k_1 > k_2$, since this implies that the pentacovalent intermediate is formed in the rate determining step of the reaction. There is no reason to expect any effect on k_1 , however. The latter point is demonstrated by the reaction of (3) and (4) with methyl iodide (Table 1).

Table 1. Rate data for the reaction between X=NPh and MeI. The reactions were performed in CDCl₃ at 25°C.

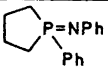
X	Conc. of MeI (mol l ⁻¹)	Conc. of phosphine imine (mol l ⁻¹)	<i>k</i> (l mol ⁻¹ s ⁻¹)
Et ₃ PhP	0.59	0.36	0.3
	0.72	0.32	0.4

The very small differences in the rates of the latter reactions can be attributed to steric effects. As to the reaction with *p*-nitrobenzaldehyde there is also the possibility that the higher rate of reaction of the phospholane derivative is due to a decrease in the rate constant k_{-1} of the backward reaction. This would imply an increase in $K = k_1/k_{-1}$ and thereby in the overall rate. At present it seems impossible to ascertain whether the observed rate difference is due to a rate increase in the second step or to an increase in $K = k_1/k_{-1}$. In view of the 3×10^3 rate increase from triphenyl- to triethylphosphine *N*-phenylimine, the finding of Johnson and Wong that electron donating substituents in the *N*-phenyl group give slower reaction rates is very interesting. It is difficult to understand, however, why the *N*-phenyl substituents are decreasing the electrophilicity of the phosphorus atom and thereby k_2 to such an extent that the rate determining step is changed, whereas electron donating substituents linked to phosphorus are not.

A possibility not considered by previous workers is a synchronized first and second step, *i.e.* the intermediate approaches towards the character of a transition state. In the Wittig reaction, intermediates have been detected and even isolated; as yet there is no experimental proof for the formation of intermediates in the present reaction of phosphine imines, however. It seems therefore that the experimental findings may be equally well explained if it is assumed that a concerted mechanism is operative, where a pentacovalent four-membered transition state is formed in a one step mechanism without

any intermediacy of betaines. In practice it is very difficult to find experimental criteria to distinguish between a concerted and a stepwise mechanism. The concerted mechanism would require a very restricted orientation of the reacting molecules, thus explaining the low reaction entropy (Table 2).

Table 2. Rate data for the reaction between phosphine imines ($R_3P=NPh$) and *p*-nitrobenzaldehyde.

Compound	Solvent	Reaction temp. °C	Rate constant ($l\ mol^{-1}\ s^{-1}$)	Activation energy (kcal mol^{-1})	ΔS at 25° (e.u.)
(1) $Ph_3P=NPh$	C_6H_6	25.0	4.9×10^{-3}	7.8	-44.9
		40.0	9.2×10^{-3}		
(2) $Ph_2EtP=NPh$	C_6H_6	25.0	4.1×10^{-2}	7.8	-40.7
		40.0	7.7×10^{-2}		
		DMF	3.6×10^{-2}		
		DMSO	7.6×10^{-2}		
		Acetone	4.7×10^{-2}		
(3) $PhEt_2P=NPh$	C_6H_6	25.0	0.67	7.8	-34.4
		40.0	1.13		
(4) 	C_6H_6	25.0	6.5^a		
(5) $Et_3P=NPh$	C_6H_6	25.0	11^a		

^a Deviations from second order kinetics presumably due to hydrolysis of the phosphine imines in the reaction mixture.

It has been argued ⁶ that the rate increase observed in ethanol and chloroform as compared to benzene is consistent with a betaine intermediate in these solvents. This is not unreasonable since polar solvents might stabilize the betaine structure. From Table 2 it is seen that the observed rate increase cannot primarily be due to increased polarity of the solvents, since the reaction rates are about the same in benzene, acetone, and dimethyl formamide. A weak rate increase is observed in dimethyl sulphoxide, but the relative insensitivity of the reaction rate on solvent polarity does not appear to be consistent with the proposed intermediacy of a betaine. A rate increase is, however, observed in solvents containing active hydrogen. The catalytic effect of a series of acids and other hydrogen bonding agents on the rate of the reaction is shown in Fig. 1. As can be seen, the catalytic effect is not a function of the acid strength of the compound containing active hydrogen atoms, but there is a fair correlation between the hydrogen bonding abilities of the compounds and the catalytic effect. Thiophenol ($pK_s=7.8$), for instance, shows no catalytic effect, whereas the much weaker acid phenol

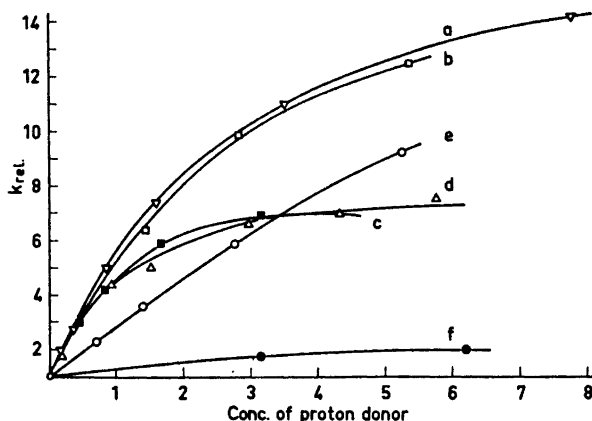


Fig. 1. Dependence of rate constant of the reaction between the phosphine imine (2) and *p*-nitrobenzaldehyde on concentration ($10^{-3} \text{ mol l}^{-1}$) of added proton donors. The proton donors are as follows: (a), CH_3COOH ; (b), $\text{C}_2\text{H}_5\text{COOH}$; (c), PhCH_2COOH ; (d), PhCOOH ; (e), PhOH ; (f), PhSH .

($\text{p}K_s = 10.0$) gives a considerable rate increase. This difference must be ascribed to the relative weakness of the SH group as a proton donor in hydrogen bonding. It seems reasonable that the rate increase with increasing amount of proton active compounds in the reaction solution is chiefly due to the stabilizing effect from hydrogen bonding between the protic media and the oxygen atom in the transition state of the reaction. A weak rate increase may also be expected from hydrogen bonding interaction between the proton acids and the carbonyl oxygen of the aldehyde.

REFERENCES

1. Staudinger, H. and Hauser, E. *Helv. Chim. Acta* **4** (1921) 861.
2. Bergmann, E. and Wolff, H. A. *Ber.* **63** (1930) 1176.
3. Horner, L. and Gross, A. *Ann.* **591** (1955) 117.
4. Appel, R. and Hauss, A. *Chem. Ber.* **93** (1960) 405.
5. Appel, R. and Schollhorn, R. *Angew. Chem.* **76** (1964) 991.
6. Johnson, A. W. and Wong, S. C. K. *Can. J. Chem.* **44** (1966) 2793.
7. Campbell, J. J., Monagle, T. W. and Foldi, V. S. *J. Am. Chem. Soc.* **84** (1962) 3673.
8. Fischer, O. *Ber.* **14** (1881) 2525.
9. Staudinger, H. and Meyer, J. *Helv. Chim. Acta* **2** (1919) 635.
10. Aksnes, G. and Frøyen, P. *Acta Chem. Scand.* **23** (1969) 2697.
11. Röchardt, C., Panse, P. and Eichler, S. *Chem. Ber.* **100** (1967) 1144.
12. Frøyen, P. *Acta Chem. Scand.* **25** (1971) 2514.
13. Frøyen, P. *Acta Chem. Scand.* *In press.*
14. Aksnes, G. and Frøyen, P. *Acta Chem. Scand.* **24** (1970) 809.

Received July 14, 1971.